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EP 0518779 A EP 0151961 A WO 91/16143 A
US 5246988 A US 4923909 A US 4728540 A
US 4393094 A

WPI Abstract Accession No 90-078628[11] & JP
02030529 A WPI Abstract Accession No 82-01230J[47]
& JP 57168934 A

(58) Field of Search

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(54) Abstract Title

Composition for treating vinyl surfaces

(57) A composition for topical treatment of vinyl surfaces for protection against environmental exposure and deterioration caused by ultraviolet light comprises from 0.01 to 20 weight percent of at least one hindered amine light stabilizer, and a delivery vehicle comprising from 0.2 to 50 weight percent of a vinyl plasticizer, and from 50 to 99.8 weight percent of a protectant base comprising an active agent selected from the group consisting of polydimethyl siloxanes, cyclomethicones and phenyl dimethicones.

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COMPOSITION FOR TREATING A VINYL SURFACE
AGAINST ENVIRONMENTAL EXPOSURE

The present application is a divisional application from UK Patent Application No 9714107.1 which claims a method for topical treatment of vinyl surfaces for protection against environmental exposure and deterioration caused by ultraviolet light.

FIELD OF THE INVENTION

This invention relates to a composition and method for topical treatment of plastics
5 for protection against environmental exposure and deterioration caused by ultraviolet light.

BACKGROUND OF THE INVENTION

Polyvinyl chloride (PVC) protectants, which have been commercialized over the years, are often comprised of solutions or emulsions of polydimethyl siloxane and
10 various other additives such as those described in U.S. Pat. Nos. 3,956,174 and 5,183,845. These products are commonly used for automotive interior and exterior PVC (vinyl) parts as well as household vinyl products to improve the appearance of the vinyl by providing gloss, and to protect the vinyl by improving durability and water repellency. While these products provide temporary improvements to vinyl
15 surfaces, testing has shown that single applications of these products do not effectively protect vinyl from extended weathering and exposure to ultraviolet (UV) light.

In order to provide a treatment for vinyl surfaces to protect from UV light, UV absorbers (UVAs) have been incorporated into silicone-based protectants, for example, as described in Canadian Patent No. 1,176,828. However, it has been found that
20 these products do not provide adequate protection from UV exposure.

U.S. Pat. No. 4,728,540 discloses the use of plasticizers for the delivery of active ingredients to vinyl films. The formulations described in this patent are designed to allow the active ingredient to be incorporated into the interior of the vinyl product.

After treatment, the vinyl must remain undisturbed for extended periods of time, up to thirty days, until the formulation is fully absorbed. Therefore, these formulations are not suited for uses where it is desired to use the vinyl within a relatively short time period after treatment, or where it may be aesthetically unacceptable to have
5 material remaining on the surface of the vinyl.

Efforts have been made to manufacture vinyl products that are resistant to the deleterious effects of ultraviolet light by incorporating additives such as UVAs and/or hindered amine light stabilizers (HALS) directly into the vinyl resin during the manufacturing process. For example, the use of hindered amines in the manufacture
10 of a variety of organic polymers is described in U.S. Pat. Nos. 4,472,547, 4,547,537, and 5,241,067. The hindered amines are incorporated into the organic polymers prior to the manufacture of shaped articles therefrom. Hindered amines have also been incorporated into polyurethane and acrylic coatings used on painted automotive surfaces, to prevent degradation of the coating itself. However, these additives do not
15 afford the long-term protection to the substrate that is needed for vinyl products that are constantly exposed to ultraviolet light, such as automobile upholstery, vinyl cartops, etc.

SUMMARY OF THE INVENTION

It is an object of the invention to provide compositions and methods for treating
20 already manufactured vinyl to protect vinyl surfaces from the effects of ultraviolet light.

It is an object of the invention to provide a method of treating a vinyl product that allows the product to be used for its intended purpose within an hour after treatment.

These and other objects and features of the invention will become apparent to those
25 skilled in the art from the following detailed description and appended claims.

The foregoing objects are achieved by a method of treating a vinyl surface comprising applying to the surface a composition that comprises from 0.01 to about 5 weight percent of at least one hindered amine light stabilizer dissolved or uniformly dispersed

in a delivery vehicle, wherein said coating is sufficiently thin without excess fluid remaining on the surface so that said vinyl surface can be used for its intended purpose within one hour after treatment.

DETAILED DESCRIPTION OF THE INVENTION

- 5 The present invention provides a composition for topical application to already manufactured vinyl. The composition protects vinyl from the deleterious effects of exposure to ultraviolet light.

The composition comprises at least one hindered amine light stabilizer that has been solubilized or emulsified in a suitable delivery vehicle. Hindered amine light
10 stabilizers (HALS) are a well known class of compounds known to prevent and retard the degradation of polymers in which they are incorporated. HALS do not absorb UV light, but are believed to act as light-stable free radical scavengers. It is believed that the HALS oxidize to form nitroxy radicals which, in turn, react with other free radicals. The complete reaction mechanism is not clearly understood, however
15 theories assume a cyclical process that regenerates the nitroxyl species, accounting for the efficacy and longevity of these materials.

HALS are commercially available from a variety of sources, including but not limited to Ciba-Geigy Corporation (e.g. Tinuvin 123, 292 or 440L), Sandoz Chemical Corporation (e.g. Sanduvor 3055, 3056 or 3058) and BASF Corporation (e.g. Uvinul
20 4050 H, or 5050 H). The formulas for various HALS are provided in U.S. Patent Nos. 5,241,067, 4,472,547, and 4,728,540, all incorporated herein by reference. Prior to the present invention, the only known method of utilizing HALS for UV protection was by the incorporation of HALS into the material to be stabilized. There is no suggestion from the prior art that HALS can provide any benefit at the surface
25 of a vinyl product. Surprisingly, it has been discovered that a topical treatment of the surface of already formed vinyl products with HALS can result in increased protection from the effects of ultraviolet light.

HALS are extremely viscous. Therefore, they are diluted with a delivery vehicle that can reduce viscosity to suitable levels and that detackifies the HALS, thus allowing

for a non-objectionable surface feel soon after application, when applied in appropriate amounts. Thus, after treatment with the compositions of the invention, the vinyl surface can be subject to normal use contact usually within 30 minutes after application (e.g. vinyl upholstery can be used). The composition can comprise from
5 about 0.01 up to about 20 weight percent HALS. At levels above 20% HALS it becomes difficult to reduce the viscosity and detackify the system. However, cost is a factor, and at levels greater than about 5 weight percent HALS there is not a significant increase in benefit with increasing amounts of HALS. The composition preferably comprises from about 0.06 to about 3 weight percent HALS, and more
10 preferably from about 0.1 to about 1 weight percent HALS.

The delivery vehicle can be any material or combination of materials that can dissolve or uniformly disperse the HALS, and be applied to the plastic without physically or chemically attacking it. Various materials including, but not limited to, polydimethyl siloxanes, cyclomethicones, phenyl dimethicones, vinyl plasticizers, and polymers
15 used in coatings such as polyurethanes and polyacrylates, meet these criteria and can be used as delivery vehicles either as solutions, solutions in other volatile carriers, or emulsions. The composition of the delivery vehicle may be selected to provide other specific attributes or benefits, including but not limited to shine, color enhancement, ozone protection, cleaning, clarity, etc.

20 Plasticizers are particularly suitable because they facilitate the handling of the HALS by readily cutting viscosity and since they comprise components of vinyl and they are nonreactive with the vinyl. Particularly preferred plasticizers are dioctyl adipate and di-n-hexyl azelate. The composition may comprise HALS with the balance being the plasticizer. In a preferred embodiment, the delivery vehicle also comprises a silicone
25 protectant base, for example an aqueous solution or emulsion of polydimethyl siloxane, which is known to condition and impart gloss to vinyl surfaces. A preferred delivery vehicle comprises from about 0.2 to about 50 weight percent plasticizer and about 50 to about 99.8% protectant base. A particularly preferred delivery vehicle comprises from about .5 to about 5 weight percent plasticizer and about 95 to about
30 99.5 weight percent protectant base. Various other additives can be incorporated into the delivery vehicle that impart additional properties to the composition. For example

antioxidants and UV absorbers can also be added. Antioxidants and UVA absorbers (e.g. TINUVIN 384, TINUVIN 328 and TINUVIN 1130, available from Ciba-Geigy Corporation) are preferably used in amounts ranging from about 0.05 to about 5 weight percent.

- 5 The composition of the present invention provides effective protection of vinyl substrates from the effects of weathering and specifically UV irradiation. The composition can be applied by spraying, with either a pump or aerosol, or by wetting a cloth, sponge or brush with the composition and wiping the surface to be treated. It is desirable to apply a sufficiently thin coating of the composition with no excess
10 fluid remaining on said vinyl surface so that the vinyl surface can be used for its intended purpose within one hour after treatment, and preferably within 30 minutes after treatment. Any excess fluid can be removed by wiping with a dry cloth. Typically, the composition is applied at a rate of about 0.05 cc composition per 100 square cm of vinyl surface to about 0.5 cc per 100 square cm. Preferably, about 0.05
15 to about 0.2 cc composition is applied per 100 square cm of vinyl surface. When HALS is incorporated directly into vinyl products during manufacturing it is used at amounts of about 0.15% relative to the total weight of the vinyl. Topical application of HALS uses significantly less HALS yet is surprisingly more effective. Thus, the present invention provides the additional benefit of being more cost effective.
- 20 In order that the invention described herein may be more fully understood, the following examples are set forth. It should be understood that these examples are for illustrative purposes only and are not to be construed as limiting the scope of the invention in any manner.

25 **Example 1: Compositions comprising HALS in a silicone protectant base/plasticizer delivery vehicle**

- The 9 formulas shown in Table I were prepared by adding hindered amine light stabilizers and other additives to a polydimethyl siloxane protectant base (which is an emulsion comprised primarily of polydimethyl siloxane, water, and emulsifiers). The following additives were used: hindered amine light stabilizers (Tinuvin 123 and 292),
30 ultraviolet absorbers (Tinuvin 384, 328 and 1130), antioxidants (Cyguard AO-711).

and plasticizers (dioctyl adipate). Amounts are in percent by weight, the protectant base forming the balance of the composition. All of the additives, which are liquids, were mixed together with moderate agitation until homogeneous. The additive mixture was then added to the liquid protectant base and mixed for 30 minutes with moderate agitation, forming an emulsion.

TABLE I

	#1	#2	#3	#4	#5	#6	#7	#8	#9
Tinuvin 123	0.20		0.25		0.06				
Tinuvin 292		0.54		0.35		0.29	0.27	0.27	1.70
Tinuvin 384	0.10	0.18			0.24		0.09	0.09	
Tinuvin 328			0.13	0.088		0.15			
Tinuvin 1130									3.30
Cyguard AO-711								0.10	
Dioctyl Adipate	1.00	2.00	1.00	1.00	1.00	1.00	1.00	1.00	5.00
Protectant Base	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%
RATING	3	3+	3	3	2	3	3	3	4

Formulas 1 to 8 were tested for their ability to protect vinyl from weathering and UV exposure. Various commercial protectant bases without any of the above additives were used as controls. The compositions were applied to vinyl samples cut from instrument panel skins that were obtained from United Technologies, a supplier of instrument panel skins to the domestic automotive industry. The compositions were applied at a rate of 0.1 cc per 15 square inches of vinyl surface, a rate determined by observing the usage of vinyl protectants by consumers on instrument panels.

The treated vinyl panels were then exposed to weathering under the conditions of the Society of Automotive Engineers (SAE) Method J-1885, Accelerated Exposure of Automotive Interior Trim Components using a Controlled Irradiance Water Cooled Xenon-Arc Apparatus. This is a standard method utilized by U.S. automakers to project resistance of interior vinyl parts to weathering. The samples were observed for signs of degradation. After 1300 kilojoules of exposure (about 700 hours), obvious visual degradation of the control samples was observed, the vinyl had begun to blacken extensively. The samples treated with HALS-containing protectants showed little or no blackening.

After visual inspection, Formulas 1 to 8 were rated for their protective abilities according to the following values (shown in Table I).

- 5 0 = no protection, blackening of vinyl
 1 = some protection, fair, slight blackening
 2 = good protection, no blackening, some discoloration
 3 = very good protection, slight discoloration
 4 = excellent protection, no change from unexposed.

Another set of samples were similarly treated and exposed. Elasticity of the samples was measured after 900 kilojoules of exposure (about 500 hours). The samples treated with HALS-containing protectants had significantly less loss of elasticity than untreated samples or those treated with control products. For reference, the Ford Motor Company specifies that instrument panel plastic materials be subject to the conditions of SAE Method J-1885 for up to 1993 kilojoules exposure (about 1000 hours).

15 Formula 9 was tested on automotive interior upholstery vinyl under the conditions of J-1885 and compared with no treatment and treatment with protectant base. Vinyl treated with Formula 9 showed no change from unexposed material after approximately 2000 kilojoules exposure, and scored a 4 in the scale described above. The protectant base-treated vinyl scored a 1, and the untreated vinyl scored a 0.

20 **Example 2: Compositions comprising HALS in solution**

Formulas 10 to 13 shown in Table II are representative compositions comprising HALS in solution.

TABLE II

	#10	#11	#12	#13
25 Cyclomethicone	79.75	78.65		75.00
Polydimethyl Siloxane, 350	20.00	20.00		10.00
Cask				
Phenyl Dimethicone				10.00
Hydrogenated Polyisobutene			95.00	
30 Dioctyl Adipate		1.00		
Di-n-hexyl Azelate			4.50	4.50
HALS	0.25	0.25	0.50	0.35
UVA		0.10		0.15

Example 3: Compositions comprising HALS in an emulsion

Formulas 14 to 19 shown in Table III are representative compositions comprising HALS in emulsion systems.

TABLE III

		#14	#15	#16	#17	#18	#19
5	Water	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%
	Emulsifier	as req'd	as req'd	as req'd	as req'd	as req'd	as req'd
	Cyclomethicone	5.00					
	Polydimethyl siloxane, 350 Cstk	10.00					
10	Polydimethyl siloxane emulsion 35%					50.00	50.00
	Hydrogenated polyisobutene			40.00			
	Diocetyl adipate		10.00		30.00		
15	Di-n-hexyl azelate	10.00		5.00			
	HALS	0.25	0.25	0.50	1.00	0.50	0.25
	UVA		0.10				

Example 4: Compositions comprising HALS in polymer systems
Formulas 20 to 22 shown in Table IV are representative polymer systems.

TABLE IV

		#20	#21	#22
	Water	8.00	4.00	54.00
5	Spensol L53, Urethane elastomer	90.00		
	Spensol L56 or L46, Urethane elastomer		20.50	
10	Aralon 840-W-39, Acrylic polymer		70.00	
	Acrylic Joncryl 95, 30%			33.00
	JA 250-3 Polysaccharide resin			11.00
15	Carbitol		4.00	
	Surface active agent	1.60	1.00	0.50
	Diethyl adipate			1.25
	HALS	0.40	0.40	0.25
	UVA		0.10	

WHAT IS CLAIMED:

1. A method of treating a vinyl surface comprising applying to said surface a coating of a composition comprising from 0.01 to about 5 weight percent of at least one hindered amine light stabilizer dissolved or uniformly dispersed in a delivery vehicle,
5 wherein the amount of said coating applied is limited to a level at which said vinyl surface is suitable for normal use contact within one hour after treatment.
2. The method of claim 1 wherein said hindered amine light stabilizer is selected from the group consisting of TINUVIN 123 and TINUVIN 292.
3. The method of claim 1 wherein said composition comprises from about 0.2 to
10 about 2 weight percent of a hindered amine light stabilizer.
4. The method of claim 1 wherein said composition further comprises from about 0.01 to about 5 weight percent of an ultraviolet absorber.
5. The method of claim 4 wherein said ultraviolet absorber is selected from the group consisting of TINUVIN 384 and TINUVIN 328.
- 15 6. The method of claim 1 wherein said delivery vehicle comprises a vinyl protectant base comprising an active agent selected from the group consisting of organopolysiloxanes, cyclomethicones, phenyl dimethicones, vinyl plasticizers, polyurethanes, polyacrylates, and combinations thereof.
7. The method of claim 6 wherein said active agent is dimethylpolysiloxane.
- 20 8. The method of claim 7 wherein said delivery vehicle further comprises from about 0.5 to about 15 weight percent of a vinyl plasticizer.
9. The method of claim 8 wherein said vinyl plasticizer is selected from the group consisting of dioctyl adipate and di-n-hexyl azelate.
10. The method of claim 1 wherein said composition further comprises an antioxidant.

11. A composition for the topical protection of already manufactured vinyl comprising from about 0.01 to about 5 weight percent of at least one hindered amine light stabilizer, about 0.5 to about 15 weight percent of a vinyl plasticizer, and about 50 to about 99.8 weight percent of a protectant base comprising an active agent
5 selected from the group consisting of polydimethyl siloxanes, cyclomethicones and phenyl dimethicones.
12. A method of treating a vinyl surface comprising applying to said surface a coating of a composition comprising from about 0.01 to about 5 weight percent of at least one hindered amine light stabilizer, about 0.5 to about 15 weight percent of a
10 vinyl plasticizer, and about 50 to about 99.8 weight percent of a protectant base comprising an active agent selected from the group consisting of polydimethyl siloxanes, cyclomethicones and phenyl dimethicones.
13. A method of treating a vinyl surface comprising applying to said surface a coating of a composition comprising from 0.01 to about 5 weight percent of at least
15 one hindered amine light stabilizer dissolved or uniformly dispersed in a delivery vehicle, wherein the amount of composition applied to said vinyl surface is from about 0.05 to about 0.5 cc per 100 square centimeters.

Amendments to the claims have been filed as follows

1. A composition for the topical protection of already manufactured vinyl comprising from 0.01 to 20 weight percent of at least one hindered amine light stabilizer, and a delivery vehicle comprising from 0.2 to 50 weight percent of a vinyl plasticizer, and from 50 to 99.8 weight percent of a protectant base comprising an active agent selected from the group consisting of polydimethyl siloxanes, cyclomethicones and phenyl dimethicones.
2. A composition as claimed in claim 1 comprising from 0.01 to 5 weight percent of at least one hindered amine light stabilizer.
3. A composition as claimed in claim 1 comprising from 0.06 to 3 weight percent of at least one hindered amine light stabilizer.
4. A composition as claimed in claim 1 comprising from 0.1 to 1 weight percent of at least one hindered amine light stabilizer.
5. A composition as claimed in claim 1 comprising from 0.2 to 2 weight percent of at least one hindered amine light stabilizer.
6. A composition as claimed in any one of the preceding claims wherein said hindered amine light stabilizer is selected from the group consisting of decanedioic acid bis(2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl) ester and bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate.

7. A composition as claimed in any one of the preceding claims wherein said delivery vehicle comprises from 0.5 to 5 weight percent of a vinyl plasticizer and from 95 to 99.5 weight percent of
5 a protectant base comprising an active agent selected from the group consisting of polydimethyl siloxanes, cyclomethicones and phenyl dimethicones.
- 10 8. A composition as claimed in any one of the preceding claims wherein the vinyl plasticizer is selected from dioctyl adipate and di-n-hexyl azelate
- 15 9. A composition as claimed in any one of the preceding claims which further comprises an ultraviolet absorber.
- 20 10. A composition as claimed in claim 9 which comprises from 0.01 to 5 weight percent of an ultraviolet absorber.
- 25 11. A composition as claimed in claim 9 which comprises from 0.05 to 5 weight percent of an ultraviolet absorber.
- 30 12. A composition as claimed in any one of claims 9 to 11 wherein said ultraviolet absorber is selected from 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid and 2-(3,5-di-tert-amyl-2-hydroxyphenyl) benzotriazole.
- 35 13. A composition as claimed in any one of the preceding claims which further comprises an antioxidant.

14. A composition as claimed in claim 13 which comprises from 0.05 to 5 weight percent of an antioxidant.
- 5 15. A composition for the topical protection of already manufactured vinyl substantially as hereinbefore described with reference to any one of examples 1, 2 or 3.



Application No: GB 9907110.2
Claims searched: 1-15 (amended)

Examiner: Richard Kennell
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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): C3T (TFA, TFB, TFC, TFD, TFE, TFX)

Int CI (Ed.6): C08J; C08K; C08L; C09D 7/12

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0518779 A (VALEO VISION), see page 3 lines 11-14 and amounts in Examples	1 at least
X	EP 0151961 A (GENERAL ELECTRIC), see page 5 lines 8-15, page 9 line 5 - page 11 line 3 and page 17 lines 5-13	-
X	WO 91/16143 A (ATOCHEM NORTH AMERICA), see page 6 lines 28 - 36, page 13 lines 5-6 and amount in Example 1	-
X	US 5246988 A (WINCKLHOFFER), see col 4 lines 53-68, and amounts in Examples (Table 4)	-
X	US 4923909 A (KUO), see col 2 lines 64-68, col 7 line 6 and col 9 lines 35-47	-
X	US 4728540 A (GASMAN), see col 4 lines 8-9, col 5 lines 27-38 and amounts in Examples	-
X	US 4393094 A (GARRETT), see col 10 lines 32-42	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



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INVESTOR IN PEOPLE

16.

Application No: GB 9907110.2
Claims searched: 1-15 (amended)

Examiner: Richard Kennell
Date of search: 16 April 1999

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Abstract Accession No 90-078628[11] & JP 02030529 A (MITSUBISHI KASEI), see abstract	-
X	WPI Abstract Accession No 82-01230J[47] & JP 57168934 A (MITSUBISHI MONSANTO), see abstract	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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